Journal of the Japan Petroleum Institute, **48**, (1), 60―66 (2005)

[Regular Paper]

Separation of Coal Tar Fractions by Solvent Extraction
—Extractant/Solvent Separation by Secondary Extraction—

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(Received August 3, 2004)

Solvent extraction was applied to the separation of tar light oil and absorption oil, and solvent recovery in the separation of these coal tar fractions by extraction with secondary oil solvent. The liquid-liquid equilibria were measured with various combinations of oil and aqueous methanol phases that occur throughout the whole extraction process. Based on the equilibrium results, a process separating absorption oil and tar light oil simultaneously with a single aqueous solvent is suggested, in which the two feed oils also act as secondary solvents for mutual separation. In the separation of feed oils by aqueous methanol solution as solvent, nitrogen heterocyclic compounds in the absorption oil and the tar light oil were extracted preferentially to other compounds including homocyclic hydrocarbons and oxygen heterocyclic compounds. In the solvent recovery in the separation of absorption oil, the aqueous extract phase containing aqueous solvent and extractants was separated by tar light oil as secondary oil solvent. In the solvent recovery in the separation of tar light oil, the aqueous extract phase was separated by absorption oil as the secondary oil solvent. The distribution coefficients were not affected by the type of oil phase of coal tar fraction and by the presence of the extractants in the aqueous phase. The distribution coefficients in all cases of oil phases of absorption oil and tar light oil could be classified into three groups: monocyclic nitrogen compounds, bicyclic nitrogen compounds, and other compounds including hydrocarbons and oxygen compounds. By integrating the two separation processes of absorption oil and tar light oil into one process separating both coal tar fractions simultaneously with a single aqueous solvent, several extractors and solvents required in the two separate processes can be eliminated.

Keywords
Coal tar, Tar light oil, Absorption oil, Solvent extraction, Aqueous methanol solution,
Nitrogen heterocyclic compounds

1. Introduction

Coal tar is a liquid by-product from the pyrolysis of coal to produce coke for the steel industry. This liquid oil mixture contains various kinds of useful compounds such as homocyclic hydrocarbons, nitrogen heterocyclic compounds, and oxygen heterocyclic compounds. These compounds are widely used as raw materials for dyes, medicines, perfumes, and many others. At present, the process for separating coal tar into these compounds consists of three principal steps: (1) distillation of coal tar into several fractions, *e.g.*, absorption oil, tar light oil; (2) separation of these fractions into two or more groups by reactive extraction with acid and base; and (3) further separation of these groups into pure compounds by distillation, crystallization, etc. Although the reactive extraction used in step (2) achieves good separation of the coal tar fractions, step (2) requires relatively high energy costs, since the solvent used in the reactive extraction is corrosive to the extractor and is difficult to recover and reuse. A large portion of the useful compounds mentioned above are now manufactured by chemical synthesis[11]. The development of simpler and more convenient methods to separate these compounds from the coal tar fractions would expand the market share of the chemical derived from coal tar.

Many methods to separate the useful compounds from coal tar have been tried. Various methods have been used in the above three steps to obtain individual nitrogen heterocyclic compounds contained in coal tar: ordinary solvent extraction; supercritical extraction; distillation; extractive distillation; azeotropic distillation; and crystallization[3]. Liquid membrane separation[8)~10], adsorption[6], etc. have also been proposed for the separation in the step (2). Ordinary solvent extraction in step (2) can preferentially extract nitrogen heterocyclic compounds from the other compounds in coal tar

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absorption oil using aqueous methanol solution as a solvent[1),2),4)].

We previously conducted experimental measurements of the liquid-liquid equilibria between the absorption oil and solvents and simple numerical simulations with these equilibrium results[5)]. This showed that an aqueous solution of methanol was preferable as the solvent instead of sulfolane, commonly adopted in the extraction of aromatic hydrocarbons from reformed petroleum fractions. The countercurrent and multistage structure of the equilibrium stages resulted in higher concentration and yield of the nitrogen compounds and hydrocarbon products. Addition of a metal salt to the solvent also enhanced extraction of the nitrogen compounds[7)]. Therefore, solvent extraction can be applied to the separation of other coal tar fractions, *e.g.*, tar light oil, consisting of nitrogen compounds, hydrocarbons, etc. On the other hand, solvent recovery, *i.e.*, the separation of extracted components and solvent components, has not been studied, although this is an essential component of the solvent extraction process.

The present study applied solvent extraction to the separation of tar light oil and absorption oil, and extraction with the secondary oil solvent to solvent recovery in the separation of these coal tar fractions. The liquid-liquid equilibria were measured with various combinations of oil and aqueous methanol phases. Based on these equilibrium results, a process separating absorption oil and tar light oil simultaneously with a single aqueous solvent using these two feed oils as secondary solvents for mutual separation is suggested.

2. Experimental

2. 1. Material Systems

The material systems are summarized in **Table 1**. Absorption oil, tar light oil, toluene and heptane were used as the oil phases, R_0. Fresh aqueous methanol solution and aqueous methanol solution equilibrated with absorption oil and/or tar light oil were used as the aqueous phases, E_0. The principal properties of tar light oil, absorption oil, toluene, heptane, and methanol are shown in **Table 2**. These material combinations occur throughout the whole extraction process as follows: absorption oil and tar light oil in MS1 and MS2 correspond to the feed oils to be separated in the extraction process; MS3-MS6 describe the systems in which the aqueous extract phases is separated into the extractants and the aqueous solvent; and absorption oil in MS7 is the model of both the feed oil and the secondary oil solvent. The compounds of interest were as follows: pyridine as a nitrogen heterocyclic compound, benzene, toluene, ethylbenzene, xylenes, indene, and naphthalene as homocyclic hydrocarbons in the tar light oil; quinoline, isoquinoline, and indole

Table 1 Material Systems of Oil Phase, R_0, and Aqueous Phase, E_0, at Initial State

No.	R_0	E_0
MS1	absorption oil	aqueous methanol solution
MS2	tar light oil	aqueous methanol solution
MS3	toluene	E_1 from run with MS1
MS4	heptane	E_1 from run with MS1
MS5	tar light oil	E_1 from run with MS1
MS6	absorption oil	E_1 from run with MS2
MS7	absorption oil	E_1 from run with MS5

Table 2 Principal Properties of Materials

			Tar light oil	Absorption oil	Toluene	Heptane	Methanol
Density		[kg·m^{-3}]	880	1054	867	684	793
Boiling point		[K]	353-443	483-559	384	372	338
Composition in mass fraction							
Nitrogen compounds							
pyridine	$x_{P,0}$	[—]	0.01	—			
quinoline	$x_{Q,0}$	[—]	—	0.09			
isoquinoline	$x_{IQ,0}$	[—]	—	0.02			
indole	$x_{IL,0}$	[—]	—	0.06			
Hydrocarbons							
benzene	$x_{B,0}$	[—]	0.25	—			
toluene	$x_{T,0}$	[—]	0.10	—			
ethylbenzene	$x_{EB,0}$	[—]	0.02	—			
xylenes	$x_{X,0}$	[—]	0.10	—			
indene	$x_{IN,0}$	[—]	0.07	—			
naphthalene	$x_{N,0}$	[—]	0.01	0.02			
1-methylnaphthalene	$x_{1MN,0}$	[—]	—	0.12			
2-methylnaphthalene	$x_{2MN,0}$	[—]	—	0.25			
biphenyl	$x_{BP,0}$	[—]	—	0.08			
Oxygen compound							
dibenzofuran	$x_{DBF,0}$	[—]	—	0.09			

as nitrogen compounds, naphthalene, 1-methylenaphthalene, 2-methylenaphthalene, and biphenyl as homocyclic hydrocarbons, and dibenzofuran as an oxygen heterocyclic compound in the absorption oil.

2. 2. Procedure

The oil phase, R_0, and aqueous phase, E_0, were brought into contact in an erlenmeyer flask with a screw cap which was shaken in a constant temperature shaker (T-22S or T-N22S, Thomas Kagaku Co., Ltd.). After equilibration, the two phases were separated into the oil raffinate phase, R_1, and the aqueous extract phase, E_1 in a separation funnel. All phases were analyzed by gas chromatography. The principal conditions of this analysis are shown in **Table 3**. Pure samples of the compounds of interest were used to identify the peaks of these components in the gas chromatograms. The details of this analysis were the same as those used in the previous work$^{5)}$. The mass fractions of the compounds of interest, toluene, heptane, and methanol were determined by gas chromatography. The mass fractions of water in the oil phases were measured with a Karl Fischer water content meter (758 KFD Titrino, Metrohm Ltd.).

2. 3. Operation Conditions

The experimental conditions are shown in **Table 4**. Our previous study showed that 48 h of contact is sufficient for equilibrium of the two phases$^{5)}$. The water content in E_0, $y_{W,0}$, and the mass ratio of the phases, E_0/R_0, were varied as shown in **Table 4**.

3. Results and Discussion

3. 1. Basic Results

3. 1. 1. Gas Chromatograms and Compositions of Coal Tar Fractions

Figure 1(a) shows the gas chromatogram of tar light oil. The retention time of tar light oil was shorter than that of absorption oil$^{5)}$. The compositions of tar light oil and absorption oil, $x_{i,0}$, are shown in **Table 2**. Both coal tar fractions consisted of nitrogen heterocyclic compounds, homocyclic hydrocarbons, and other compounds. Almost all compounds in the tar light oil were monocyclic and those in the absorption oil were bicyclic.

3. 1. 2. Gas Chromatogram of Aqueous Phase Equilibrated with Tar Light Oil

An example gas chromatogram of aqueous methanol phases equilibrated with tar light oils ($y_{W,0} = 0.5$, $E_0/R_0 = 2$) is depicted in **Fig. 1(b)**. The ratios of the peak height of pyridine relative to peaks of other components in the gas chromatogram of the aqueous phase were larger than the ratios in the chromatogram of tar light oil, showing that pyridine was transferred into the aqueous phase preferentially to other components.

Table 3 Apparatus and Conditions of Analysis by Gas Chromatography

Gas chromatograph		GC-17AAF ver.3 (Shimadzu Corp.)
Column		ULBON Capillary Column HR-1 (Shinwa Chemical Ind., Ltd.)
inner diameter	[m]	2.5×10^{-4}
length	[m]	30
Carrier gas		N_2

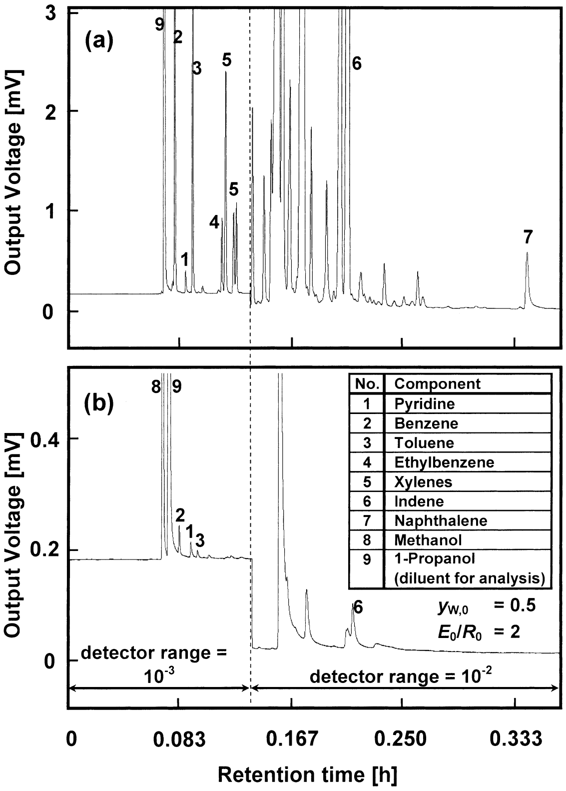

Fig. 1 Gas Chromatograms of (a) Tar Light Oil and (b) Aqueous Phase Equilibrated with Tar Light Oil

Table 4 Experimental Conditions

Mass of oil phase, R_0	[kg]	0.01-0.08
Mass fraction of water in aqueous phase E_0, $y_{W,0}$	[—]	0.3-0.7
Mass ratio of oil phase and aqueous phase, E_0/R_0	[—]	0.25-4.0
Shaking time	[h]	48
Amplitude of shaking	[m]	0.01
Frequency of shaking	[h^{-1}]	7200
Temperature	[K]	303

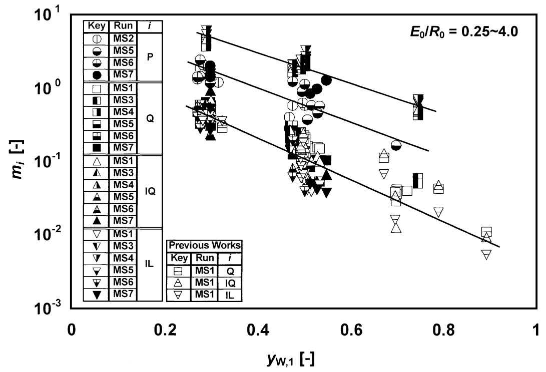

Fig. 2 Distribution Coefficients of Nitrogen Compounds

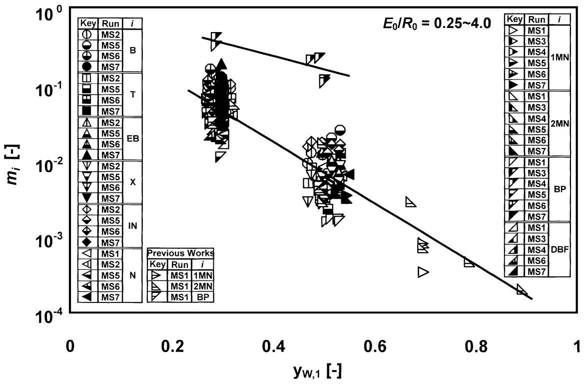

Fig. 3 Distribution Coefficients of Hydrocarbons and Oxygen Compound

3. 2. Numerical Relationships

The material balance of component i during the phase contact is given by

$$R_0 \cdot x_{i,0} - R_1 \cdot x_{i,1} = E_1 \cdot y_{i,1} - E_0 \cdot y_{i,0} \quad (1)$$

with the masses and compositions of the respective phases. The left side of the equation represent the mass decrease of component i in the oil phase and the right side, the increase in the aqueous phase. Since Eq. (1) was favorably satisfied for all compounds in all cases, the results obtained in this study were consistent. The distribution coefficient of component i, m_i, was defined by the following equation:

$$m_i = y_{i,1}/x_{i,1} \quad (2)$$

with the compositions of oil and aqueous phases at equilibrium.

3. 3. Contact with Fresh Aqueous Methanol Solutions

The distribution coefficients calculated by Eq. (2) in the cases where E_0 was the fresh aqueous methanol solution are shown as MS1 and MS2 in **Figs. 2**-**4**. The distribution coefficients of nitrogen compounds (**Fig. 2**) were higher than those of other compounds (**Fig. 3**) in MS1. These results reconfirmed that absorption oil could be separated into nitrogen compounds and other compounds by extraction with aqueous methanol solution. The distribution coefficients of pyridine, a nitrogen compound, were large relative to those of other compounds in MS2 as well as MS1 (**Fig. 2**). Therefore, pyridine and other compounds in tar light oil can be separated, similarly to the case of absorption oil. These differences between the distribution coefficients were attributed mainly to the relatively high polarity of nitrogen compounds compared to the other compounds.

As shown in **Fig. 4**, the distribution coefficient of methanol was so high that dissolution of methanol into oil phase would not be so serious in the separation of both absorption oil and tar light oil ($x_{M,1} = 0.01$-0.07 at $y_{W,1} = 0.3$-0.7, $E_0/R_0 = 0.25$-4). The mass fractions of water in the tar light oil phase before and after the extraction, $x_{W,0}$ and $x_{W,1}$, were approximately 10^{-3}, and those in absorption oil were 10^{-4}. The transfers of water from the aqueous phases to the oil phases were, consequently, negligible for both coal tar fractions.

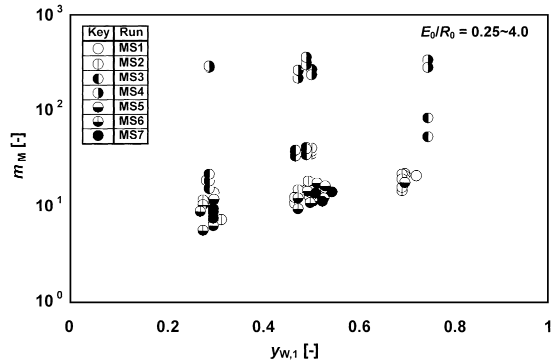

Fig. 4 Distribution Coefficients of Methanol

The previous results[5),7)] for MS1 are also shown in **Figs. 2**, **3**, and **4**. The results in this study agreed well with those in the previous studies. The distribution coefficients of the components in coal tar fractions decreased with increasing water concentration in the aqueous phases, mainly due to the increasing polarity of the aqueous phase. Some components could not be detected in E_1, where $y_{W,1}$ was high. The effect of water concentration in the aqueous phase on the distribution coefficients of methanol was insignificant (**Fig. 4**). The mass ratio of aqueous phase to oil phase, E_0/R_0, did not affect the distribution coefficients in any case.

3. 4. Contact with Equilibrated Aqueous Methanol Solution

Generally, the solvent in an extraction process is selected based on several criteria as follows: (1) ability to extract the desired component(s) from the opposite phase; (2) insolubility in the opposite phase; (3) easy separation from extractants (*e.g.*, differences between boiling points of solvent and extractants for separation by distillation); and (4) availability and low cost.

Table 5 Comparisons of Single Processes and Combined Process for Separation of Tar Light Oil (TLO) and Absorption Oil (AO)

	Single process		Combined process
	TLO	AO	TLO and AO
Extractor for			
main extraction	1	1	2
reverse-extraction	1	1	—
Distillator	1	1	2
Solvent stream for			
main extraction	1	1	1
reverse-extraction	1	1	—

Based on criterion (3), toluene and heptane were first selected as models for secondary oil solvents to compare solvents of higher and lower polarities. The distribution coefficients in MS3 and MS4 are shown in **Figs. 2**, **3**, and **4**. The oil phases were toluene and heptane, and the aqueous phase was methanol solution equilibrated with absorption oil. The distribution coefficients in MS4 in which the oil phase was heptane were higher than those in MS3 with toluene (**Figs. 2** and **3**), that is, the extractants in the aqueous phase transferred into toluene more than into heptane. The distribution coefficient of toluene was higher than that of heptane ($m_T = 0.0002\text{-}0.003$ at $y_{W,1} = 0.3\text{-}0.5$, $E_0/R_0 = 0.25\text{-}1$), so toluene dissolved in the aqueous phase more than heptane. Toluene is preferable as a secondary oil solvent for criterion (1), whereas heptane is superior for criterion (2).

As criterion (4) is also important in a practical process, use of other coal tar fractions, which are readily available, as the secondary oil solvent is preferable in the separation of coal tar fractions. In accordance with criteria (1) and (2) as well as (4), absorption oil and tar light oil were then selected as solvents. The distribution coefficients in MS5, MS6, and MS7 are shown in **Figs. 2** to **4**. In MS5 and MS6, the oil phases were tar light oil and absorption oil, and the aqueous phases were methanol solutions equilibrated with absorption oil and with tar light oil. Absorption oil was used as the oil phase and the methanol solution phase was equilibrated with absorption oil and tar light oil beforehand, in MS7. The distribution coefficients with polar oil phases were smaller than those in MS4 in which the oil phase was heptane (**Figs. 2** to **4**). The distribution coefficients of the compounds other than methanol were almost equivalent to those in MS3 with toluene (**Figs. 2** and **3**), whereas those of methanol were lower than in MS3 (**Fig. 4**). The coefficients in MS5, MS6, and MS7 were very similar. The distribution coefficients in MS2 and MS5 were equivalent. The coefficients in MS6 and MS7 agreed with those for MS1.

Consequently, the distribution coefficients in all cases using oil phases of absorption oil and tar light oil (**Figs. 2** and **3**) could be classified into three groups: monocyclic nitrogen compounds (pyridine), bicyclic nitrogen compounds (quinoline, isoquinoline, indole), and other compounds including hydrocarbons (benzene, naphthalene, etc.) and oxygen compounds (dibenzofuran).

3. 5. Separation Processes of Absorption Oil and Tar Light Oil

The process of tar light oil (or absorption oil) extraction consists of the following steps: (1) separation of tar light oil (or absorption oil) into nitrogen compounds and other compounds by extraction with aqueous methanol solution; (2) separation of extractants and aqueous solvent by extraction with absorption oil (or tar light oil) as a secondary oil solvent; and (3) separation of extractants and the secondary oil solvent by distillation. The principal equipments and solvents required for each separation process are listed in **Table 5**. In single process for separation of tar light oil (or absorption oil), two extractors and two solvents are required for steps (1) and (2) and a distillator is necessary for step (3) as shown in **Fig. 5**. Therefore, four extractors, four solvents, and two distillators are needed for the separation of both absorption oil and tar light oil.

Since the distribution coefficients of the compounds were not affected by the type of oil phase of coal tar fraction and by the presence of extractants in the aqueous phase as shown in this study, separation of the feed oil and the extractants and aqueous solvent can be carried out simultaneously with a single extractor. The boiling ranges of absorption oil and tar light oil are sufficiently different as shown in **Table 2**. Therefore, the separation processes of absorption oil and tar light oil can be integrated into a combined separation process as shown in **Fig. 6**. In this process, absorption oil and tar light oil are both the feed oils and the secondary oil solvents for mutual separation. **Table 5** lists the equipments and solvents for this integrated process as well. Only two extractors and only one solvent are necessary to obtain the four product streams of monocyclic nitrogen compounds, bicyclic nitrogen compounds, monocyclic hydrocarbons, bicyclic hydrocarbons, etc. By this integration of the single processes, two extractors and three solvents can be elimi-

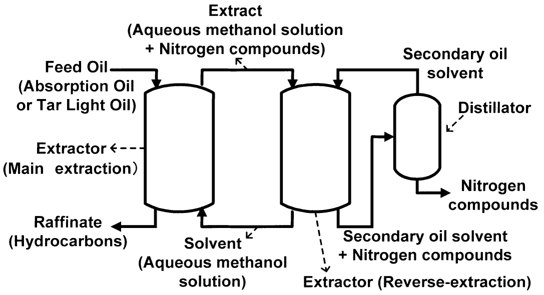

Fig. 5 Single Separation Process of Tar Light Oil or Absorption Oil

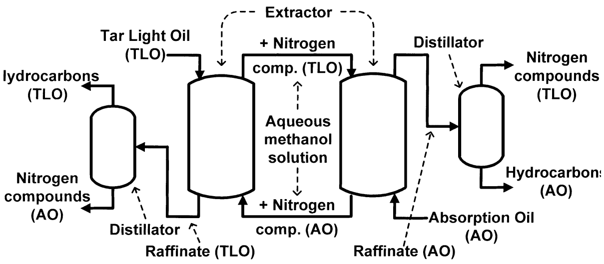

Fig. 6 Integrated Separation Process of Tar Light Oil and Absorption Oil

nated. Furthermore, criterion (2) for solvent selection, insolubility of the secondary solvent in the aqueous solvent phase, is no longer required.

Countercurrent extraction, reflux, selection of operating conditions, and other factors require further studies for the practical use of this proposed process.

4. Conclusion

Nitrogen compounds in the absorption oil and the tar light oil were extracted preferentially to other compounds by the aqueous methanol solution. The aqueous extract phase containing aqueous solvent and extractants in the absorption oil separation were separated by the tar light oil acting as secondary oil solvent. In the tar light oil separation, the secondary oil solvent for solvent recovery was absorption oil. The distribution coefficients were not affected by the type of oil phase of coal tar fraction and by the presence of extractants in the aqueous phase. The distribution coefficients in all cases of oil phases of absorption oil and tar light oil could be classified into three groups: monocyclic nitrogen compounds, bicyclic nitrogen compounds, and other compounds including hydrocarbons and oxygen compounds. By integrating the two separation processes of absorption oil and tar light oil into one process separating both coal tar fractions simultaneously with a single aqueous solvent, several extractors and solvents required in the two separation processes can be eliminated.

Acknowledgment

Absorption oil and tar light oil were provided by JFE Chemical Corporation. A part of this work was supported by a Grant-in-Aid for Scientific Research (B) (No.13,650,826) from the Japan Society for the Promotion of Science.

Nomenclatures

E : mass of aqueous phase [kg]
m : distribution coefficient [—]
R : mass of oil phase [kg]
x : mass fraction in oil phase [—]
y : mass fraction in aqueous phase [—]
<Subscripts>
0 : initial state
1 : equilibrium state
1MN : 1-methylnaphthalene
2MN : 2-methylnaphthalene
B : benzene
BP : biphenyl
DBF : dibenzofuran
EB : ethylbenzene
i : component i
IL : indole
IN : indene
IQ : isoquinoline
M : methanol
N : naphthalene
P : pyridine
Q : quinoline
T : toluene
X : xylenes
W : water

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要　　旨

溶媒抽出によるコールタール留分の分離ー第2の抽出による抽出物／溶媒成分の分離ー

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コールタール留分であるタール軽油と吸収油の分離，また第2の油性溶媒による溶媒回収に溶媒抽出を適用した。この抽出プロセスで起こりうる様々な油相とメタノール水溶液相の系に関する液液平衡を測定した。測定した平衡関係に基づいて，一つの水溶性溶媒を用いて吸収油とタール軽油を同時に分離するプロセスを提案した。このプロセスでは，両原料は互いの分離における第2の油性溶媒でもある。メタノール水溶液を溶媒とした両原料の分離では，吸収油とタール軽油中に含まれる含窒素複素環式化合物は同素環式炭化水素や含酸素複素環式化合物などの他の化合物よりも優先的に抽出された。吸収油の分離における溶媒回収では，第2の油性溶媒としてタール軽油を用いて水溶性の抽出相を水溶性溶媒と抽出物に分離した。タール軽油の分離においては第2の油性溶媒として吸収油を用いた。成分の分配係数は系のコールタール留分の種類，また水溶液中に含まれる抽出物によって影響されなかった。すべての系において成分の分配係数は大きく三つのグループに分類して，単環の含窒素化合物，二環の含窒素化合物と炭化水素や含酸素化合物などの他の化合物という順であった。吸収油とタール軽油のそれぞれの分離プロセスを一つの水溶性溶媒による両コールタール留分の同時分離プロセスに統合することによって，それぞれの分離プロセスに必要な抽出装置と溶媒のいくつかが除去できる。

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